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## Physical vapor deposition

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**Physical vapor deposition** (PVD) is a technique used to deposit thin films of various materials onto various surfaces (e.g., of semiconductor wafers) by physical means, as compared to chemical vapor deposition.

PVD is used in the manufacture of items including semiconductor devices, aluminized mylar for balloons and snack bags, and coated for metalworking.

Leading manufacturers of PVD tools include Applied Materials (~78.1% market share in 2004), Novellus (~6.2% market share in 2004), and Unaxis (~4.8% market share in 2004). Leading consumers of PVD tools include Intel, Samsung, and Taiwan Semiconductor.

Variants of PVD include

- [Evaporative deposition](#)
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- [Pulsed laser deposition](#)
- High velocity oxygen fuel

See [thin-film deposition](#) for a more general discussion of this class of manufacturing technique.

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## Definition of physical vapor deposition (PVD)

1. a process whereby films of material, usually metals, are deposited by physical means, for example, evaporation and sputtering. [SEMATECH]

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# CONCISE ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

1985

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urethane (see Urethane polymers) industry, which consumes over 85% of the world's phosgene output. Polycarbonates (qv) consume ca 6%, and the remaining 9% is used for herbicides (qv).

EDGAR E. HARDY  
San Diego State University

• *Chemical Safety, Data Sheet SD-95*, Chemical Manufacturer's Association, Washington, D.C., Revised 1978.

H. Babad and A.G. Zeiler, *Chem. Rev.* 73(1), 75 (1973).

• W.F. Diller, *J. Occup. Health* 20, 189 (Mar. 1978).

PHOSPHAMIDON. See Insect control technology.

## PHOSPHORIC ACIDS AND PHOSPHATES

Phosphates may be defined as compounds containing four phosphorus-oxygen (P=O) linkages. Compounds containing discrete, i.e., monomeric  $\text{PO}_4^{3-}$  ions are known as orthophosphates or simply phosphates, linear condensed P-O-P chains as polyphosphates, cyclic rings as metaphosphates, branched polymeric materials and cage anions as ultraphosphates. Stoichiometrically, phosphates have been represented as combinations of oxides, eg,  $\text{H}_3\text{PO}_4$  as  $\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4$  as  $\text{P}_2\text{O}_5 \cdot 2\text{Na}_2\text{O} \cdot \text{H}_2\text{O}$  (see Table 1).

### Phosphoric Acid

Phosphoric acid,  $\text{H}_3\text{PO}_4$ , is the highest value inorganic acid marketed in the United States, and the second largest in terms of volume. Its main use is in the manufacture of phosphate salts, mainly for fertilizers (qv).

Phosphoric acid is a tribasic acid in which the first hydrogen is strongly ionizing ( $K_1 = 7.1 \times 10^{-3}$ ), the second moderately weak ( $K_2 = 6.3 \times 10^{-8}$ ), and the third very weak ( $K_3 = 4.4 \times 10^{-13}$ ). Aside from its acidic behavior, phosphoric acid is relatively inert at room temperature. It is not reduced by strong reducing agents below 350–400°C; at elevated temperature it reacts with most metals and their oxides.

Pure phosphoric acid is a white crystalline solid (monoclinic), mp 42.35°C; the crystalline hemihydrate melts at 29.25°C. Properties of aqueous solutions are given in Table 2.

Phosphoric acid is manufactured either by the wet process or the furnace process. Over 90% of the U.S. production is made by the former, by digesting phosphate rock (apatite form) with sulfuric acid. The phosphoric acid is separated from the resulting calcium sulfate slurry by filtration. Chemical precipitation and solvent extraction are the main methods of purification; crystallization and ion exchange are also used.

Table 1. Traditional Classification of Sodium Phosphates

Oxide ratio, R ( $\text{Na}_2\text{O} + \text{H}_2\text{O}_{\text{comp}}$ ): $\text{P}_2\text{O}_5$	Designation	General formula	Structure
> 3	phosphate + metal oxide (includes double salts and solid solutions)		mixtures
3	phosphate or orthophosphate, $n \leq 3$	$\text{Na}_n\text{H}_{3-n}\text{PO}_4$	one phosphorus atom
$3 > R > 2$	mixture of ortho- and pyrophosphates		
2	pyrophosphate, $n \leq 4$	$\text{Na}_n\text{H}_{4-n}\text{P}_2\text{O}_7$	two phosphorus atoms
$2 > R > 1$	polyphosphates, $n = 2, 3, 4, \dots$	$\text{Na}_{n-2}\text{P}_n\text{O}_{3n+1}$	linear chains
1	metaphosphates, $n = 3, 4, 5, \dots$	$\text{Na}_n(\text{PO}_3)_n$	cyclic or extremely long chains
$1 > R > 0$	ultraphosphates, $0 < x < 1$	$(x\text{Na}_2\text{O})\text{P}_2\text{O}_6$	cross-linked chains and/or rings
0	phosphorus pentoxide	$(\text{P}_2\text{O}_5)_n$	$\text{P}_4\text{O}_{10}$ or continuous structures

Table 2. Physical Properties of Aqueous Solutions of Phosphoric Acid

Concentration, wt %		Density, 25°C, g/cm <sup>3</sup>	Bp, °C	Fp, °C	Viscosity, mPa·s (= cP) at		
$\text{H}_3\text{PO}_4$	$\text{P}_2\text{O}_5$				20°C	60°C	100°C
0	0	0.997	100.0	0	1.0	0.48	0.30
5	3.62	1.025	100.1	-0.8	1.1	0.54	0.33
10	7.24	1.053	100.2	-2.1	1.2	0.61	0.38
20	14.49	1.113	100.8	-6.0	1.6	0.79	0.48
30	21.73	1.182	101.8	-11.8	2.2	1.0	0.62
50	36.22	1.333	108	-44.0	4.3	1.8	1.1
75	54.32	1.573	135	-17.5	15	4.8	2.4
85	61.57	1.685	158	21.1	28	8.1	3.8
100	72.43	1.864	261	42.35	140	25	9.2
105	76.10	1.925	>300	16.0	600	70	19
115	83.29	2.044	>500			1500	250

The double-neutralization process is used to purify phosphoric acid during the production of large-volume detergent-builder phosphates.

In the furnace process, elemental white (yellow) phosphorus is burned in excess air; the resulting phosphorus pentoxide is hydrated, the heats of combustion and hydration are removed, and the phosphoric acid mist is collected. The processes are called wetted-wall, water-cooled, or air-cooled, depending on the protection of the combustion-chamber wall.

A potential environmental problem is created by the burning of phosphorus, which produces a persistent white cloud of phosphorus pentoxide and phosphoric acid droplets of such high obscuring power that it is used as a screening smoke by the military (see Chemicals in war). Neither precipitators nor Venturi scrubbers reduce the pentoxide content to a level acceptable in states with low plume-opacity regulations (see Air pollution); therefore, high efficiency mist eliminators are now standard practice.

Elemental phosphorus produced by the electrothermal process is a distilled product of high purity, which yields phosphoric acid pure enough for most industrial uses. The high heat of combustion of phosphorus [3.05 MJ/mol (730 kcal/mol)] can be recovered for process use such as evaporation of water from dilute phosphate solutions.

Furnace-grade phosphoric acid is used in metal treatment, refractories, catalysts, and food applications.

### Phosphates

Both mono- and disodium phosphates are prepared commercially by neutralization of phosphoric acid with sodium carbonate or hydroxide. Trisodium phosphate (TSP) is crystallized from a wet-mix solution.

Monosodium phosphate is used as a pH buffer in acid-type cleaners, in boiler-water treatment, as a precipitant for polyvalent metal ions, and as an animal-feed supplement. Mixtures of mono- and disodium phosphates are used in textile and food processing (see Water, industrial water treatment), in the preparation of glazes and enamels, and in leather tanning, textile dyeing, and detergents. Trisodium phosphate is strongly alkaline and is a constituent of many heavy-duty cleaning compositions. The hypochlorite complex is used in disinfectants, scouring powders, and dishwashing formulations (see Bleaching agents).

In addition to the three simple potassium phosphates, the  $\text{K}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  system contains a number of crystalline hydrates and double salts.

The piezoelectric effect of monopotassium phosphate has led to its use in sonar systems and other electronic applications; it is also used in buffering systems and paper processing.

Tri- and dipotassium phosphates are marketed both as a solid and in a 50% solution; their main uses are as corrosion inhibitors in ethylene glycol antifreeze formulations and in coffee creamers.

Although thermally unstable, ammonium phosphates are present as solid phases in the  $\text{NH}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  system from 0 to 75°C. Mono- and diammonium phosphates (MAP and DAP, respectively) are the world's leading phosphate fertilizers. Other applications are related to flame retardation and fire extinguishing (see Flame retardants).

The alkaline-earth phosphates are less soluble than those of the alkali metals. Apatite (calcium phosphate) ores supply the basic raw material for the production of phosphorus and its derivatives. Commercial calcium phosphates, produced from furnace-grade phosphoric acid, constitute the second largest volume phosphate salts. Most calcium phosphates are mixtures of several salts; their composition depends on the manufactur-

ing conditions. Uses include fertilizers, animal feeds, food applications, and dentifrices.

The tertiary metal phosphates are of the formula  $MPO_4$ , where  $M = B, Al, Ga, Fe$ , and  $Mn$ . The boron and aluminum compounds are used as refractories.

Phosphate salts of heavy metals are insoluble in water. Zinc phosphate is used in dental cements (see Dental materials). Chromium and zinc phosphates provide corrosion protection and paint adhesion in some metal-treating applications. Mixed sodium-aluminum phosphates are utilized in some food applications.

### Rolyposphoric Acids

The only clearly defined crystalline compositions of the  $H_2O-P_2O_5$  system are three forms of phosphoric acid and their hemihydrates, pyrophosphoric acid, and crystalline  $P_4O_{10}$ . Amorphous condensed phosphoric acids are hygroscopic; they may be viscous, oily, gummy, and may consist of a mixture of glassy and crystalline materials.

Linear-polyphosphoric acids are strongly hygroscopic and undergo viscosity changes and hydrolysis to less complex forms when exposed to moist air (see Table 3). Upon dissolution in excess water, hydrolytic degradation to phosphoric acid occurs.

Pyrophosphoric (diphosphoric) acid,  $H_4P_2O_7$ , crystallizes in two forms (mp = 54.3 and 71.5°C); acid salts are known. Tripolyphosphoric (tripolyphosphoric) acid,  $H_5P_3O_{10}$ , occurs in varying amounts as a component of condensed phosphoric acids containing more than ca 72%  $P_2O_5$ .

The largest use of polyphosphoric (superphosphoric) acids is as an intermediate in the production of liquid fertilizers. Condensed acids of 82–84%  $P_2O_5$  are employed as catalysts in the petroleum industry. Polyphosphoric acid is also used as a dehydrating agent and in the production of phosphoric esters and agricultural chemicals.

### Polyphosphates

The condensed phosphates are derived from phosphates by the loss of water. These materials range from simple diphosphates (pyrophosphates) to long-chain polymeric structures with molecular weights in the millions ( $10^6$ ).

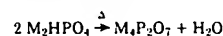
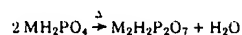
Polyphosphates are resistant to chemical attack, but are susceptible to hydrolysis. Short-chain polyphosphates hydrolyze without the concurrent formation of cyclic metaphosphates; in this respect they differ from the long-chain acids. Many polyphosphates form water-soluble complex ions, a phenomenon called sequestration (see Chelating agents). This property forms the basis for the water-treatment and detergent applications.

Table 3. The Linear Polyphosphoric Acids of General Formula  $H_{n+2}P_nO_{3n+1}$

Formula	Wt % $P_2O_5$	Structure	Prefix	Number of dissociated hydrogen atoms	
				Strong	Weak
$H_3PO_4$	72.42	$\begin{array}{c} O \\    \\ HO-P-OH \\   \\ OH \end{array}$	mono- (ortho)	1	2
$H_4P_2O_7$	79.76	$\begin{array}{c} O \quad O \\    \quad    \\ HO-P-O-P-OH \\   \quad   \\ OH \quad OH \end{array}$	di- (pyro)	2	2
$H_5P_3O_{10}$	82.54	$\begin{array}{c} O \quad O \quad O \\    \quad    \quad    \\ HO-P-O-P-O-P-OH \\   \quad   \quad   \\ OH \quad OH \quad OH \end{array}$	tri- (tripoly)	3	2
$H_6P_4O_{13}$	84.01	$\begin{array}{c} O \quad O \quad O \quad O \\    \quad    \quad    \quad    \\ HO-P-O-P-O-P-O-P-OH \\   \quad   \quad   \quad   \\ OH \quad OH \quad OH \quad OH \end{array}$	tetra-	4	2
$H_{n+2}P_nO_{3n+1}$		$\begin{array}{c} O \quad O \quad O \quad O \quad O \\    \quad    \quad    \quad    \quad    \\ HO-P-O-P-O-P-O-P-OH \\   \quad   \quad   \quad   \quad   \\ OH \quad OH \quad OH \quad OH \quad OH \end{array}$	poly	n	2

### Pyrophosphates

The simplest linear condensed phosphates ( $M_{n+2}P_nO_{3n+1}$ , where  $n = 2, 3, 4, \dots$ ) are pyrophosphates ( $M_4P_2O_7$ ). A water molecule is eliminated from condensed orthophosphates:

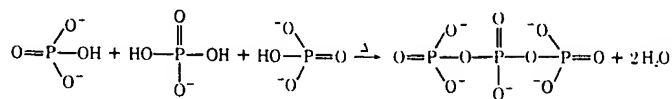


Insoluble pyrophosphates are obtained by treating a soluble salt of the desired cation with a sodium pyrophosphate solution.

Tetra- and disodium pyrophosphates (sodium acid phosphate) are prepared by thermal dehydration of di- and monosodium orthophosphate, respectively. Tetrasodium pyrophosphate is used as a builder in detergent and cleaning formulations (see Surfactants and detergent systems), in food applications (see Food additives), and as a deflocculant in drilling muds, dyes and inks. Sodium acid pyrophosphate is used as a leavening and chelating agent.

Calcium pyrophosphate exists in three polymorphic modifications; they form progressively upon dehydration of calcium hydrogen phosphate dihydrate. Calcium pyrophosphates are used primarily as abrasives in fluoridated toothpaste (see Dentifrices).

The tripolyphosphate anion,  $P_3O_{10}^{5-}$ , consists of triply condensed  $PO_4^{3-}$  tetrahedra:



Sodium tripolyphosphate (STP, pentasodium triphosphate),  $Na_5P_3O_{10}$ , occurs as the anhydrous forms I (STP-I) (thermodynamically stable) and II (STP-II), the low temperature form; the transition temperature is  $417 \pm 8^\circ C$ . They are differentiated by x-ray diffraction, IR, Raman spectra, and the temperature-rise test (ASTM D 501, 30). A hexahydrate forms by the addition of either anhydrous form to water or by the hydrolysis of sodium trimetaphosphate,  $(NaPO_3)_3$ . STP is produced commercially by calcination of a mixture of mono- and disodium phosphates.

The solubility and hydration behavior of STP are of particular importance in its industrial applications. As a builder for synthetic detergents, STP is the largest-volume phosphate salt for purposes other than fertilizers.

Thermal dehydration of monosodium phosphate gives rise to numerous condensed polyphosphates, eg, Graham's, Madrell's, and Kurrol's salts.

In the manufacture of phosphate salts, phosphoric acid is treated with a base, eg, carbonate, hydroxide, or ammonia, to form a solution or slurry. Most phosphates crystallize readily from solution and are separated by conventional techniques; the solutions or slurries are often evaporated to dryness.

The phosphate glasses are manufactured in refractory-type furnaces, where they are heated to  $1000^\circ C$ , then quenched rapidly to a solid glass; trade names are used for glasses of only slightly different composition.

Sodium tripolyphosphate (90–95% pure) is manufactured by drying and subsequent calcination of a solution or slurry with a  $Na_2O/P_2O_5$  mole ratio of 1.67, corresponding to two mol disodium phosphate and one mole monosodium phosphate. Calcining conditions are less critical than drying conditions; combinations of dryer/calcining units are available.

Disodium phosphate,  $Na_2HPO_4$ , is marketed as the dihydrate and the anhydrous salt. Tetrasodium pyrophosphate,  $Na_4P_2O_7$ , is obtained by calcination of disodium phosphate or any of its hydrates. Commercial manufacture is similar to that of STP, except that the final  $Na_2O/P_2O_5$  ratio is adjusted with  $NaOH$ ; the same equipment can be used.

Chlorinated TSP, the second largest volume sodium phosphate salt, is a complex mixture approximating  $(Na_3PO_4 \cdot 11H_2O)_4 \cdot NaOCl$ . It is made by the addition of sodium hypochlorite solution to a hot concentrated

together at a 30° angle. On contact, an arc is struck and melts the wire ends. Compressed air or nitrogen drives the liquid metal forward to the work. As the arc is broken, the wires are advanced to repeat the process. The arc temperature (ca 3800°C) causes deposition of molten droplet ca 3–8 times faster and with more fluidity than oxyacetylene flame-spray units. Because all of the heat is used to melt metal, this method is most energy-efficient.

**Plasma:** The plasma spraying process utilizes the available energy in a controlled electric arc to heat gases to  $\geq 8000^\circ\text{C}$ . The low voltage arc is ignited between a water-cooled tungsten cathode and a cylindrical water-cooled copper anode (see Plasma technology).

Although expensive as a spray method, the plasma spraying process is suitable for specialty coating and has wide usage commercially, particularly for thermal-barrier coatings on jet-engine blades and diesel-engine parts.

**Laser coating.** Laser power is applied to produce sprays of powdered material for coating purposes (see Lasers). Powder particles can be accelerated in the laser beam and melted before striking the substrate material where rapid solidification takes place. Power from a 25-kW  $\text{CO}_2$  laser is directed into a suitable chamber and focused on the substrate surface. A carrier gas, eg, helium, is used to transport powdered material through a gold-plated water-cooled nozzle which projects powder into the laser beam. The accelerated molten particles impact on the substrate and, depending on the power density at the substrate, either coat the substrate with a quenched structure or are incorporated into a region of the substrate that has been melted by the beam. Solid particles, eg, carbides, in the latter process can be incorporated into the molten matrix with little dissolution, thereby producing a modified surface region that is up to 1 mm thick and impregnated with hard particles for wear resistance (see Lasers).

**Electrostatic powder coating.** A relatively new application of an old technique is the electrostatic deposition of powders, eg, Al, Cr, Ni, and Cu. Cleaned strip or sheet is electrostatically coated with metal powder, cold-rolled to compact the coating, and sintered by heating to develop a bond to the steel. The principal advantage is the protection provided at 500°C in service, eg, heating appliances, automotive exhaust systems, and heat exchanger (see Powder coatings).

**Slurry coatings.** Metallic coatings can be applied simply by applying powders of the desired metal or alloy in a paint medium and by brushing, dipping or spraying it onto the basis material. The coating is cured and then fired, during which time the organic portion vaporizes and the metallic particles fuse to form a dense, metallurgically bonded coating. Slurry coatings, because of the multiple handling steps and the extensive heat treatments required, tend to be expensive, and uses are limited to specialty coatings.

#### Mechanical and Liquid-Metal Cladding

Metallic coatings also can be applied by mechanical methods where the coating material is forced into intimate contact with the basis metal such that the forces at the interface disrupt and disperse the boundary oxide films existing on each of the constituent metals. Formation of a metallurgical bond may be augmented by mechanical attachment and thermal interdiffusion. Metallic coatings also can be melted into place by a weld-surfacing or casting operation. These techniques generally are applied to large, heavy basis metals in the form of plates or large forgings and usually produce quite thick coatings in comparison to other types of processes. Weld surfacing is a cost-effective method.

The selection criterion for a given method of producing a composite plate is the required thickness of the desired protective material and the thickness of the basis material to which it is applied. If 1 cm is adequate, the solid coating (cladded) alloy often is used alone. For a basis material  $> 1\text{-cm}$  and up to 6-cm thick, roll-bonding techniques are used. Explosion bonding is most often used when the basis metal thickness is ca 6–8 cm (see Metallic coatings, explosively clad metals). Beyond a 10-cm basis-metal thickness, only weld-overlay techniques or electrosag-casting techniques are practical.

**Electrosag cladding.** A technique similar to the submerged-arc process, but which works with more massive equipment and produces much thicker coatings, is the electrosag weld-overlay coating process. The heat

energy necessary to melt the basis metal and the filler alloy is generated by electrical current in a molten, electrically conducting slag which also purifies and protects the filler metal as it advances through the slag layer into the molten pool. The molten slag and metal pool are held against the basis metal by water-cooled copper retainers, which must conform to the contour of the object to be clad. One application for this process is in the refurbishing of mill rolls which can be performed on ESR (electrosag remelted) ingot-production units with only minor change. Electrosag is ca 25% more efficient than submerged arc, largely because of the lower labor requirements of the former process. It is applicable only to large objects using equipment repetitively.

#### Chemical Coatings

**Chemical vapor deposition (CVD).** Chemical vapor deposition is the gas-phase analogue of electroless plating (qv): CVD is catalytic, occurs on surfaces, and involves a chemical reduction of a species to a metallic or compound material which forms the coating; the reactions are temperature dependent but occur at much higher temperatures than in plating.

Chemical reactions utilized in CVD are reduction reactions, displacement reactions, and disproportionation reactions. These generally require temperatures from 500 to 1200°C and often as high as 1500°C. For example, a CVD process may involve a metal carrier compound, ie,  $\text{SiCl}_4$ , which is reduced by a gaseous reducing agent such as  $\text{H}_2$  to deposit a metallic coating, or on the other hand, may occur by thermal decomposition of an unstable compound such as  $\text{Ni}(\text{CO})_4$ , nickel carbonyl, into its parts, one of which is a metal, which subsequently forms the deposit as pure metal, or in some cases as a compound by reaction with another gas species (see Film deposition techniques).

Chemical vapor deposition coatings tend to be purer than non-CVD-produced coatings. Control of chemical composition is a matter of controlling the gaseous reactants entering the reactor; graded coatings and mixed (sequential) coatings are possible through selection of appropriate gases. Control of the nucleation and growth of coating-metal crystallites is a matter of great importance because it affects strongly chemical properties of the composite. Recently, plasma-assisted CVD has resulted in effective processing of some semiconductor materials at much lower temperatures, eg, ca 300°C, by using energy from the plasma to promote the desired reaction.

#### Vacuum Coatings

In vacuum deposition, the desired coating metal is transferred to the vapor state by a thermal or ballistic process (sputtering) at low pressure. The vapor is expanded into the vacuum toward the surface of the precleaned basis metal. Diffusion-limited transport and gas-phase pre-nucleation of the coating material is avoided by processing entirely in a vacuum that is sufficiently low to ensure that most of the evaporated atoms arrive at the basis metal without significant collision with background gas. This usually requires a background pressure of 0.665–66.5 mPa (0.005–0.5  $\mu\text{m Hg}$ ). At the basis metal, the arriving atoms of coating metal are condensed to a solid phase. The condensation process involves surface migration, nucleation of crystals, growth of crystals to impingement, and often renucleation. Thermal sources based on resistance ( $I^2R$ ) heating, induction heating, electron-beam heating, and laser irradiation have been used to vaporize the coating material. These processes are physical vapor-deposition techniques, ie, thermal energy raises the material to its melting point or above, whereupon it is vaporized by evaporation and adiabatic expansion. If the evaporated coating metal is made to intercept atoms or ions of a special background gas, with which it may react to form a compound, and then strikes the basis metal, the process is reactive evaporation. Other vapor-generating methods such as sputtering and ion implantation (qv) may also be used. The use of r-f sputtering allows oxides and other compounds to be vaporized. Because of the specialized equipment involved, vapor-deposited coatings tend to be expensive, but for some uses this is not unattractive because of the properties of the resulting composite. Ion implantation, though quite expensive, is attractive for use in mitigating wear in a number of industrial applications. Recent work has shown ion implantation produces a reduction of 400–1000 times in wear of metallic